

# Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

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REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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TABLE 12.—Summary statistics for nitrogen (N) and phosphorus (P) concentrations in water from the Upper Floridan aquifer, calculated from selected water analyses and reported as elemental N or P

Species		Number of samples	Concentration, in milligrams per liter					
			Maximum	75 percentile	Median	Mean	25 percentile	Minimum
Total - N	(F) <sup>1</sup>	26	4.7	0.80	0.52	1.07	0.31	0.08
Ammonia (NH <sub>4</sub> )-N	(F)	44	2.1	0.52	0.29	0.40	0.15	0.01
Organic (Org)-N	(F)	35	4.6	0.37	0.20	0.45	0.05	0
Nitrite (NO <sub>2</sub> )-N	(F)	112	0.06	<0.01	0	<0.01	0	0
Nitrate (NO <sub>3</sub> )-N	(F)	328	3.16	0.09	0	0.14	0	0
NH <sub>4</sub> + Org (KJD)-N	(F)	36	4.7	1.03	0.55	0.83	0.33	0.08
NO <sub>2</sub> +NO <sub>3</sub> -N	(F)	56	3.0	0.05	0.05	0.19	0.01	0
Total - N	(UF)	273	8.67	1.61	1.45	1.48	1.18	0.06
NH <sub>4</sub> -N	(UF)	293	2.1	1.25	1.0	0.86	0.41	0
Org-N	(UF)	275	1.2	0.35	0.2	0.24	0.07	0
NO <sub>2</sub> -N	(UF)	331	0.55	<0.01	<0.01	0.01	<0.01	0
NO <sub>3</sub> -N	(UF)	332	7.6	0.02	0	0.31	0	0
KJD-N	(UF)	270	2.54	1.5	1.34	1.11	0.84	0
NO <sub>2</sub> +NO <sub>3</sub> -N	(UF)	260	7.78	0.08	0.01	0.37	<0.01	0
Total - P	(F)	34	2	0.07	0.02	0.10	<0.01	0
Orthophosphate (PO <sub>4</sub> )-P	(F)	83	2	0.05	0.02	0.05	<0.01	0
Total - P	(UF)	270	1.8	0.08	0.06	0.07	0.03	0
PO <sub>4</sub> -P	(UF)	261	1.2	0.08	0.05	0.06	0.02	0

<sup>1</sup> F, filtered water sample; UF, unfiltered (whole) water sample.

ground-water flow is very sluggish. Aluminum concentrations are likely very low, possibly controlled by (1) the solubility of gibbsite or (2) the alteration of kaolinite to mixed-layer clays (smectites).

#### NUTRIENTS

The occurrence of the principal nutrients, nitrogen (N) and phosphorus (P) species, in the Upper Floridan aquifer was investigated by retrieval of all N and P data available for the 601 wells used to describe the major ion chemistry. A total of 648 analyses (from 591 wells) of various N and P species were compiled into a data set and statistically analyzed using procedures available in SAS (SAS Institute, 1979). Table 12 reports summary statistics for both total and dissolved nutrient-species concentrations. The 648 analyses contained some qualified values. Especially common were concentrations reported as less than a threshold value (detection limit). For "less than" qualified values, a concentration of one-half the threshold value was substituted before any statistical tests were performed. The data in table 12 show that except for dissolved nitrate, the preponderance of analyses of N and P species were made on whole water samples; thus, bacteria in the water were analyzed, along with any trace solids (minerals) containing N or P forms. These whole-water analyses are probably representative of "available" N, however, since microorganisms can easily reduce and assimilate organic N. The orthophosphate (PO<sub>4</sub>) in organic material (or minerals) is readily assimilated in any case.

The data shown in table 12 indicate that low concentrations of P occur throughout the Upper Floridan aquifer; 75 percent of the samples contained less than 0.1 mg/L of P. At these low concentrations, P dissolved in ground water may be limiting to the growth of bacterial populations in the aquifer, if mineral sources of P are not available. Bacteria contain mole ratios of carbon(C):N:P of 47.3:7.3:1 (Fenchel and Blackburn, 1979, table III, p. 16). This means that to assimilate, for example, 0.05 mg/L of P completely, the bacterial population needs only 0.17 mg/L of N and 0.92 mg/L of C. In the Upper Floridan aquifer, the median concentration of NH<sub>4</sub> nitrogen in more than 290 samples was 1.0 mg/L (table 12) and the median concentration of dissolved organic carbon in 48 samples was 4.0 mg/L (table 18). Both are well above the amounts required for a bacterial population to assimilate 0.05 mg/L of P, the median concentration of P, even if other sources of N and C were not available. Bacterial assimilation of the median concentration of P calculated for filtered water samples (0.02 mg/L, table 12), that is, P in "true" solution, would require even less N or C in solution.

The sources of the various N and P species in the Upper Floridan aquifer are not well defined over the aquifer's areal extent. As described previously, the Upper Floridan aquifer contains trace amounts of phosphate minerals in many areas; the overlying Hawthorn Formation contains economic concentrations of phosphate minerals in southwestern and north-central Florida. Wherever recharge through the Hawthorn can

occur, dissolved-phosphate concentrations may increase in the Upper Floridan aquifer. In unconfined areas, both phosphate and nitrate dissolved from fertilizers or dissolved in other manmade discharges may also enter the Upper Floridan. Although some generalizations can be made concerning nutrient distributions within the aquifer system, the reader should use local data (whenever possible) to evaluate bacterial growth conditions in the Upper Floridan aquifer.

Because N species are present in moderate concentrations in the ground water and no mineral sources of N exist within the Floridan aquifer system, the occurrence of individual species and total concentration of N were examined to determine the likely sources (and sinks) of the element. Three hypotheses were tested by statistical analysis of the nutrient data set:

1. The aquifer system is in a state of natural dynamic equilibrium, where total N input (through precipitation) equals output (via ground-water discharge) from the system. Individual N species may not be distributed uniformly within the system, but total N concentrations are similar in recharge and discharge areas. No trend of increasing or decreasing N concentrations over time is observed in recharge or discharge areas.
2. Man's activities at land surface have affected the input levels of N through leaching of fertilizers and land application of wastes from industrial or municipal water-treatment plants. The aquifer system is not in dynamic equilibrium; some individual species and total N concentrations in unconfined recharge areas are significantly higher than in discharge areas. Nutrient analyses of ground water in unconfined recharge areas show a time trend of increasing total N concentrations; nutrient analyses from discharge areas do not show any time trends.
3. Man's activities have affected the input levels of N by leaching of fertilizers and spreading of wastes, and through direct recharge of the aquifer system with nitrogen-rich water via drainage or disposal wells (point sources). The system is not in dynamic equilibrium; some individual species and total N concentrations are significantly higher in both confined and unconfined recharge areas than in confined discharge areas. Nutrient analyses of ground water in recharge areas show a time trend of increasing total N concentrations; nutrient analyses from discharge areas do not show any time trends.

To perform statistical tests of these hypotheses, each nutrient analysis was designated by the location of the well sampled as a confined or unconfined area (fig. 11); each analysis was also designated by location of the well

sampled as an area of recharge or discharge through diffuse upward leakage (fig. 12). Statistical tests were performed on P species, as well as N species, as an independent test of the time-trend aspects of the three hypotheses.

Before testing the three hypotheses, the problem of missing values of total N (TOT-N) and total P (TOT-P) had to be overcome. Although 273 measurements of TOT-N were available in the original data set (table 12), these analyses were made of water samples from only 21 wells. Review of the data set revealed that nitrate N ( $\text{NO}_3\text{-N}$ ) had been measured in filtered water samples (F) from the most wells—328 samples from 134 wells (table 12)—in the original data set. The most frequently measured nitrogen species— $\text{NO}_3\text{-N}$  in unfiltered water samples—was measured in 332 samples from 46 wells (table 12). To obtain the greatest areal coverage of nutrient data for hypothesis testing, missing concentrations of total N and P species were estimated from dissolved concentrations for each water analysis according to the following regression equations:

$$\text{PO}_4\text{-P} = 0.99235 * \text{PO}_4\text{-P(F)}, r^2 = 0.830, n = 23, \quad (\text{N1})$$

$$\text{NO}_3\text{-N} = 1.01186 * \text{NO}_3\text{-N(F)}, r^2 = 1.000, n = 37, \quad (\text{N2})$$

$$\text{NO}_2 + \text{NO}_3\text{-N} = 0.98855 * (\text{NO}_2 + \text{NO}_3\text{-N(F)}), r^2 = 0.999, n = 7, \quad (\text{N3})$$

$$\text{KJD-N} = 1.05631 * \text{KJD-N(F)}, r^2 = 0.897, n = 7, \quad (\text{N4})$$

$$\text{NH}_4\text{-N} = 1.01822 * \text{NH}_4\text{-N(F)}, r^2 = 0.996, n = 11, \quad (\text{N5})$$

where  $r^2$  is the coefficient of determination ( $r$  is commonly called the correlation coefficient) and  $n$  is the degree of freedom, which is the number of water samples used in the regression minus the number of parameters in the regression equation, and KJD-N is organic nitrogen as determined by the Kjeldahl method. The symbols for the independent variables (N and P species) are the same as shown in table 12. The intercepts of the regression lines were not included in equations N1 through N5 because the intercepts were not significantly different from zero at the 95 percent confidence level. The  $r^2$  statistic is a measure of how much variation occurs in the dependent variable between the values calculated by the regression equations and the observed values. When  $r^2$  is equal to 1.000, the correlation between the regression equations and the observed values is perfect. For  $n$  less than 5, the model is probably an untrustworthy predictor of the dependent variable, regardless of the value of  $r^2$ .

After estimating concentrations of total species, models to estimate missing TOT-N and TOT-P concentrations from total species concentrations were developed by using single- and multiple-regression techniques. Estimates of TOT-N were made preferentially by two-variable equations, whenever values of both independent

TABLE 13.—Mean and standard deviation of nutrient concentrations in selected water samples from wells in different hydrologic settings in the Upper Floridan aquifer

[In milligrams per liter, unless otherwise indicated]

Nutrient species	Hydrologic setting			
	Unconfined recharge area	Unconfined discharge area	Confined recharge area	Confined discharge area
TOT-N	m=1.53, s=0.90, n=110 <sup>1</sup>	m=1.27, s=0.25, n=43	m=1.48, s=0.78, n=9	m=1.36, s=0.68, n=330
NO <sub>3</sub> -N	m=0.71, s=1.09, n=132	m=0.07, s=0.15, n=102	m=0.26, s=0.79, n=16	m=0.10, s=0.56, n=372
NO <sub>2</sub> +NO <sub>3</sub> -N	m=0.99, s=1.23, n=81	m=0.14, s=0.19, n=12	m=0.05, n=1	m=0.11, s=0.72, n=214
KJD-N	m=0.13, s=0.28, n=46	m=1.42, s=1.70, n=9	m=0.65, n=1	m=1.26, s=0.44, n=242
NH <sub>4</sub> -N	m=0.05, s=0.07, n=52	m=0.28, s=0.22, n=10	m=0.64, n=1	m=0.97, s=0.40, n=262
TOT-P	m=0.03, s=0.04, n=71	m=0.21, s=0.60, n=14	m=0.03, s=0.04, n=6	m=0.07, s=0.12, n=256
PO <sub>4</sub> -P	m=0.03, s=0.04, n=45	m=0.17, s=0.52, n=14	m=0.03, s=0.04, n=6	m=0.06, s=0.09, n=255

<sup>1</sup> m, population mean; s, population standard deviation; n, number of observations.

variables were available. For both TOT-N and TOT-P, the regression model with the largest  $r^2$  value was used, whenever the independent variable(s) was (were) available. The regression models used to estimate missing values of TOT-N and TOT-P are shown below:

$$\text{TOT-P} = 1.14744 \cdot \text{DIS-P} - 0.00891, r^2 = 0.996, n = 7 \quad (\text{N6})$$

$$\text{TOT-P} = 1.21716 \cdot \text{PO}_4\text{-P}, r^2 = 0.972, n = 267 \quad (\text{N7})$$

$$\text{TOT-N} = 1.00221 \cdot (\text{NO}_2 + \text{NO}_3\text{-N}) + 1.00442 \cdot \text{KJD-N} - 0.01451, r^2 = 0.999, n = 219 \quad (\text{N8})$$

$$\text{TOT-N} = 1.01636 \cdot \text{NO}_3\text{-N} + 1.01557 \cdot \text{KJD-N} - 0.01449, r^2 = 0.999, n = 264 \quad (\text{N9})$$

$$\text{TOT-N} = 1.00124 \cdot (\text{NO}_2 + \text{NO}_3\text{-N}) + 1.12585 \cdot \text{NH}_4\text{-N} + 0.10098, r^2 = 0.966, n = 221 \quad (\text{N10})$$

$$\text{TOT-N} = 1.00238 \cdot \text{NO}_3\text{-N} + 1.12241 \cdot \text{NH}_4\text{-N} + 0.14350, r^2 = 0.945, n = 270 \quad (\text{N11})$$

$$\text{TOT-N} = 0.73328 \cdot (\text{NO}_2 + \text{NO}_3\text{-N}) + 1.14418, r^2 = 0.722, n = 221 \quad (\text{N12})$$

$$\text{TOT-N} = 0.69936 \cdot \text{NO}_3\text{-N} + 1.22294, r^2 = 0.660, n = 270, \quad (\text{N13})$$

where DIS-P is dissolved phosphorus.

Clearly, the regression equation for predicting TOT-N (eq. N8) should have a coefficient of determination of 1.000 and a zero intercept. The calculated coefficients and nonzero intercept in equation N8 are due to estimating concentrations of total species from concentrations of dissolved species. Regression equations for estimating concentrations of TOT-N from either KJD-N or NH<sub>4</sub>-N alone had  $r^2$  less than 0.005 and were not used.

Standard parametric methods (analysis of variance) were not used to test the three hypotheses, because the data for the seven nutrient species were highly skewed—the lowest concentrations had the highest number of observations. Instead, the Kruskal-Wallis non-parametric test (SAS, 1979, p. 331–334) with an approximate significance test (chi square) was employed. The

concentration data for the seven nutrient species were subdivided into four subgroups on the basis of hydrologic setting of the well; for example, nutrient concentrations measured in a water sample from a well in an unconfined recharge area of the Floridan aquifer system were added to the “unconfined recharge” subgroup. The mean, standard deviation, and number of samples of each nutrient species in each subgroup are given in table 13. The results of comparing concentrations of the nutrient species subgroup by subgroup, using the Kruskal-Wallis procedure, are given in table 14.

The results of statistical tests of the N-species data indicate that total concentrations of N are similar in recharge and discharge areas and in confined and unconfined areas, and between cross-combinations of the different hydrogeologic settings. Comparison of the total concentration of N in unconfined recharge areas with the total concentration of N in confined discharge areas also showed no significant differences (table 14, pt. IV). The individual N species did exhibit significant differences, however, which hint at biogeochemical processes occurring in the Upper Floridan aquifer. The results shown in table 14 indicate that nitrate reduction occurs practically everywhere in the aquifer system. Even unconfined areas show changes in N species from more oxidized to more reduced forms between recharge and discharge areas. The quantitative effects of ground-water flow and aquifer confinement on changes in N species concentrations cannot be learned from these statistical tests, because changes in N species concentrations along individual flow paths were not calculated. The results of statistical tests on data from the entire aquifer system suggest, however, that there is a quantitative decrease in oxidized N species and a quantitative increase in reduced N species from recharge areas to discharge areas. These biochemical transformations in the aquifer system should be more carefully studied and quantified, because both fermentative nitrate reduction and denitrification can affect the carbonate chemistry of the ground water, especially the isotopic composition of the dis-

TABLE 14.—Effect of hydrologic setting on nutrient concentrations measured in selected water samples from wells in the Upper Floridan aquifer

Part I:				
Nutrient	Hydrologic setting of well			
	Unconfined	Confined	Recharge	Discharge
TOT-N	N.S. <sup>1</sup>	N.S.	N.S.	N.S.
NO <sub>3</sub> -N	+	—	+	—
NO <sub>2</sub> +NO <sub>3</sub> -N	+	—	+	—
KJD-N	—	+	—	+
NH <sub>4</sub> -N	—	+	—	+
Part II:				
Nutrient	Hydrologic setting of well			
	Recharge		Discharge	
	Unconfined	Confined	Unconfined	Confined
TOT-N	N.S.	N.S.	N.S.	N.S.
NO <sub>3</sub> -N	+	—	N.S.	N.S.
NO <sub>2</sub> +NO <sub>3</sub> -N	— <sup>2</sup>	—	N.S.	N.S.
KJD-N	—	—	N.S.	N.S.
NH <sub>4</sub> -N	—	—	—	+
Part III:				
Nutrient	Hydrologic setting of well			
	Unconfined		Confined	
	Recharge	Discharge	Recharge	Discharge
TOT-N	N.S.	N.S.	N.S.	N.S.
NO <sub>3</sub> -N	+	—	N.S.	N.S.
NO <sub>2</sub> +NO <sub>3</sub> -N	+	—	—	—
KJD-N	—	+	—	—
NH <sub>4</sub> -N	—	+	—	—
Part IV:				
Nutrient	Hydrologic setting of well			
	Unconfined recharge		Confined discharge	
TOT-N	N.S.		N.S.	
NO <sub>3</sub> -N	+		—	
NO <sub>2</sub> +NO <sub>3</sub> -N	+		—	
KJD-N	—		+	
NH <sub>4</sub> -N	—		+	

<sup>1</sup> N.S., not significant at the 99 percent confidence level; +, group higher than alternative hydrologic setting; —, lower than alternative hydrologic setting.

<sup>2</sup> Analysis of variance not made, because sample population was less than 5.

solved carbonate species. Recent work by Plummer and others (1983) has shown methods for quantifying the effects of biochemical reactions involving sulfate on the  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$  content of the ground water in the Floridan aquifer system. Considering the widespread occurrence of nitrate reduction implied by these results, efforts should be made to gather the necessary chemical and isotopic data to quantify both the amount of nitrate reduction occurring in the Upper Floridan aquifer and the effect of nitrate reduction on the carbon isotopic composition of the ground water.

To test for time trends in the selected nutrient data, a nonparametric test was employed. Water-quality data that are skewed (serially correlated) and exhibit seasonality can be examined for time trends using a procedure called the seasonal Kendall test, developed by Hirsch and

others (1982). As previously stated, the selected nutrient data were highly skewed. A test of seasonality using standard analysis of variance of monthly group means (other time groups were also tested) showed that at the 98-percent confidence level the nutrient analyses from the 591 selected wells had significantly different monthly means; that is, the data exhibited seasonality. A non-parametric test, the Wilcoxon two-sample test (SAS, 1979, p. 331), also indicated seasonality at the 95-percent confidence level. Having determined skewness and seasonality in the data set, tests for serial correlation were considered unnecessary before applying the seasonal Kendall test.

The seasonal Kendall test has been written into a SAS procedure by Crawford and others (1983). Although they warn that the test is "not robust against serial correlation," these authors (p. 50) suggest that for ground water, the use of fewer than 12 groups (monthly) "will help avoid serious problems due to serial correlation." Therefore, time-trend tests were performed using the seasonal Kendall test with the number of data groups ranging from 12 to 2. The results of testing for time trends with concentration data grouped variously from monthly to semiannually were not predictable. For a nutrient species in the same hydrologic setting, the probability that no trend existed might increase uniformly, decrease uniformly, increase to a peak and then decrease, or be erratic as the number of groups was reduced. The possibility that significant differences in concentrations of nutrient species might be observed on a monthly or bimonthly interval seems remote for the Floridan aquifer system, if the system is subjected to areally diffuse, low-concentration inputs (hypotheses 1 and 2). The seasonal Kendall test results are reported in table 15 for only quarterly and semiannual groups, because these results might be significant.

The results of testing the selected nutrient data for time trends were inconclusive. A positive time trend for P species was indicated only for the entire data set and for the confined discharge areas. Possibly the "significant" trends in P concentrations are an artifact of changes in ground-water sampling procedures during the period of record (1965–83). During the period 1973–80, nutrient samples were chilled to 4 °C but no chemical preservatives were added to the sample; from 1965 to 1973, and beginning again in late 1980, mercuric chloride was added to nutrient samples prior to chilling to 4 °C. These changes in preservation technique, accompanied by a gradually increasing number of samples collected from year to year, may account for the very slight positive trend in P concentrations. The very small negative slopes calculated for N species in different hydrologic settings probably also are the result of these changes in sampling technique. The positive slope calcu-

TABLE 15.—Trend probabilities (Tp) and estimates of slope (S) calculated from nutrient concentrations in selected water samples from wells in different hydrologic settings in the Upper Floridan aquifer

[Samples were collected during the period 1965–83]

	TOT-N	NO <sub>3</sub> -N	NO <sub>2</sub> +NO <sub>3</sub> -N	KJD-N	NH <sub>4</sub> -N	TOT-P	PO <sub>4</sub> -P
<u>Entire data set:</u>							
<u>Quarterly</u>							
Tp <sup>1</sup>	0.437	0.000	0.000	0.027	0.920	0.009	0.001
S <sup>2</sup>			–0.008	–0.031		0.001	0.002
<u>Semiannually</u>							
Tp	0.862	0.010	0.000	0.641	0.482	0.013	0.004
S			–0.010			0.002	0.002
<u>Unconfined recharge areas:</u>							
<u>Quarterly</u>							
Tp	0.156	0.000	0.308	0.908	0.720	0.179	0.656
S		0.105					
<u>Semiannually</u>							
Tp	0.735	0.002	0.318	0.471	0.801	0.495	0.876
S		0.055					
<u>Unconfined discharge areas:</u>							
<u>Quarterly</u>							
Tp	0.282	0.414	0.341	0.308	0.221	1.000	1.000
S							
<u>Semiannually</u>							
Tp	0.336	0.269	0.368	0.221	0.452	0.656	0.458
S							
<u>Confined recharge areas:</u>							
<u>Quarterly</u>							
Tp	0.165	0.012	N.C. <sup>3</sup>	N.C.	N.C.	1.000	1.000
S		–0.009					
<u>Semiannually</u>							
Tp	0.112	0.023	N.C.	N.C.	N.C.	1.000	1.000
S		–0.015					
<u>Confined discharge areas:</u>							
<u>Quarterly</u>							
Tp	0.464	0.000	0.000	0.014	0.285	0.004	0.001
S			–0.002	–0.029		0.001	0.002
<u>Semiannually</u>							
Tp	0.961	0.002	0.001	0.132	0.170	0.030	0.017
S			–0.003			0.002	0.002

<sup>1</sup> Trend probabilities greater than 0.05 are not considered significant; that is, the null hypothesis that no trend exists is not rejected for Tp>0.05.

<sup>2</sup> Slope estimates are indicated in units of milligrams per liter per year only for significant trend probabilities. The actual values of S are not given when S was several orders of magnitude lower than the analytical detection limit.

<sup>3</sup> N.C. - Tp and S were not computed because sample population less than 5.

lated for nitrate concentrations measured in unconfined recharge areas is, however, too large to be an artifact of sampling technique. The observed trend of increasing nitrate concentrations in ground water in unconfined recharge areas of the Upper Floridan aquifer probably results from increased development (residential, agricultural, and commercial) in the region during the period 1965–83. It is uncertain why only nitrate shows a significant time trend in the unconfined recharge areas; perhaps the regression equations for estimating the other N species, especially TOT-N, are sufficiently inexact to mask any trends. A more likely explanation is that the N

species measured are not the predominant N species produced by bacterial reduction of nitrate occurring in unconfined recharge areas. In the Upper Floridan aquifer, dissimilative nitrate reduction to N<sub>2</sub> (denitrification) may be a quantitatively important process, but its gaseous product is not measured routinely. Restating comments made previously, efforts should be made to study the processes and effects of nitrate reduction occurring in the Upper Floridan.

In summary, the results of the statistical tests of the selected nutrient data indicate that the aquifer system may be in dynamic equilibrium with respect to N: no



significant differences in total N were observed between unconfined or confined areas, or between recharge and discharge areas, or in cross-combinations of the different hydrologic settings. However, a significant time trend of increasing nitrate concentrations was determined in the unconfined recharge areas. The results of these tests, therefore, do not preclude the possibility of the dynamic nonequilibrium hypotheses 2 or 3 being true. It is also possible that the flow system is in dynamic equilibrium and that man's activities have affected N concentrations in the unconfined recharge areas. Denitrification and loss of  $N_2$  gas may be quantitatively important in removing the N added as nitrate in the unconfined recharge areas, but further studies are needed to test this hypothesis. Although this study was inconclusive in describing the N chemistry and the effects of nonpoint pollution on the geochemistry of the aquifer system, the effects of point sources of pollution on N chemistry in the aquifer system have previously been documented. Some of these site-specific studies are cited in the later section on trace organic contaminants.

#### TRACE METALS AND ENVIRONMENTAL ISOTOPES

The criteria for selection of water-quality data to describe the common ions were modified to obtain the statistical analyses discussed in this section. In order to have a larger sample population, all trace metal analyses dated 1970 or later from wells and springs in the Upper Floridan aquifer were used for the trace metals interpretations, regardless of well depth or areal coverage. Only wells that might be associated with disposal of wastes were excluded; this was done to avoid potential point-source bias in the regional description of the "natural" variability in minor element concentrations. Table 16 gives statistical summaries of trace metal concentrations in the Upper Floridan aquifer; figure 35 shows the general location of the wells and springs that were sampled. Although figure 35 shows many sampling sites, most wells and springs were analyzed for only iron and manganese; the areal distribution of samples for most other trace metals is very limited. Filtration of water samples through 0.45- $\mu$ m filters affects trace metals in the same manner as it does aluminum. As discussed by Hem (1985, p. 130-131), many particulate metal hydroxides that are small enough to pass through a filter of this size have adsorbed trace metals. When the filtered sample is acidified, the particulates and sorbed metals are dissolved, and analysis reports concentrations of the trace metals as though they were actually in solution in ground water. Interpretation of these "dissolved" element data by assuming mineral solubility control over trace metal concentrations may be unproductive or misleading.

Most trace element analyses of water from the Upper Floridan aquifer have been made on samples from drinking water supplies, and the summary data indicate that almost all samples contained trace metal concentrations lower than national drinking water standards (U.S. Environmental Protection Agency, 1975, 1980, 1981). Drinking water supplies in the Upper Floridan aquifer tend to produce only good-quality water, and analyses of water samples from these sources may not be representative of the entire aquifer system. Although sampling over the entire region has not been done, the absence of natural sources of many trace metals strengthens the presumption that very low concentrations should be present in unsampled areas.

Selenium (Se) concentrations greater than 0.005 mg/L in table 16 may be due to random errors in chemical analysis, especially Se analyses made prior to 1975 (R.J. Pickering, U.S. Geological Survey, written commun., 1981). Prior to 1975, the Geological Survey analyzed Se by the colorimetric diaminobenzidine method (Brown and others, 1970), which may have contained (undocumented) positive interferences. Analyses of Se made by the Geological Survey after 1975 have used the atomic absorption with hydride generation method (Skougstad and others, 1979); very few concentrations greater than 0.001 mg/L of Se have been reported since use of this method began. The Geological Survey has examined its historical data on Se concentrations in surface water, but no regional pattern exists either areally or temporally. At this time (1986), the Geological Survey considers that, for water samples analyzed by its laboratories before 1975, reported concentrations of dissolved and total Se greater than 0.005 mg/L are probably incorrect, and concentrations of dissolved Se greater than 0.001 mg/L are questionable.

The few high trace metal concentrations reported in table 16 may be related to very local conditions, possibly influenced by local contaminant sources or well construction. The low solubility of minerals composed of trace metal cations and sulfide, oxide, or hydroxide anions should limit dissolved trace metal concentrations to very low levels in most of the Upper Floridan aquifer. In areas where the Upper Floridan contains dissolved oxygen, many trace metals form insoluble oxides or hydroxides in the mildly alkaline ground water. Even trace elements that form soluble oxyanions tend to absorb strongly to particulate metal hydroxides and become "immobilized." In areas where reducing conditions are present, hydrogen sulfide is prevalent and will react with many trace metals to form insoluble metal sulfides. Thus, while contamination may locally produce abnormally high concentrations of dissolved trace metals, (bio)chemical reactions within the Upper Floridan aquifer cause many metals to precipitate from solution near the contaminant

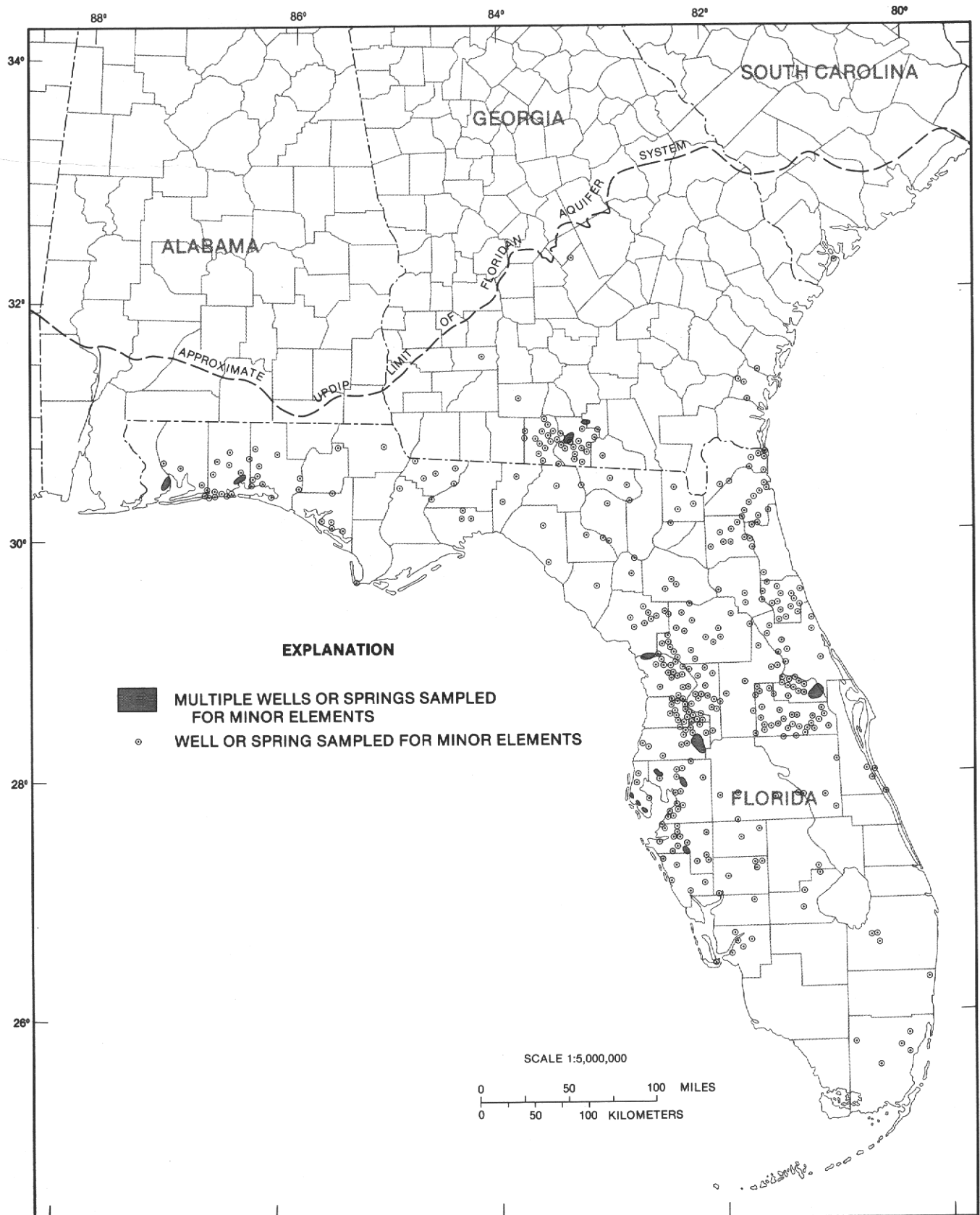


FIGURE 35.—Wells and springs in the Upper Floridan aquifer sampled for minor elements.



TABLE 16. — *Summary of selected minor element concentrations in water from the Upper Floridan aquifer*

[In milligram per liter. Dashes indicate calculation not performed]

Constituent	Number of samples	Maximum	95-percentile	75-percentile	Median	25-percentile	5-percentile	Minimum	Remarks
Arsenic, dissolved	198	0.035	0.015	0.004	0.001	0.001	0.000	0.000	<sup>1</sup> MCL 0.05
Arsenic, total recoverable	135	.044	.008	.002	.001	.001	.000	.000	
Barium, dissolved	19	.12	.12	.10	.10	.020	.000	.000	MCL 1.0
Barium, total recoverable	38	.30	.21	.10	.10	.10	.10	.10	
Boron, dissolved	98	4.2	.64	.12	.040	.020	.000	.000	
Boron, total recoverable	10	.46	.46	.11	.040	.027	.020	.020	
Cadmium, dissolved	169	.020	.005	.002	.000	.000	.000	.000	MCL 0.01
Cadmium, total recoverable	130	.008	.003	.002	.000	.000	.000	.000	
Chromium, dissolved	130	.020	.011	.003	.000	.000	.000	.000	MCL 0.05
Chromium hexavalent, dissolved	69	.010	.005	.000	.000	.000	.000	.000	
Chromium, total recoverable	118	.15	.041	.020	.020	.010	.010	.000	
Cobalt, dissolved	69	.040	.003	.000	.000	.000	.000	.000	
Cobalt, total recoverable	105	.010	.005	.002	.000	.000	.000	.000	
Copper, dissolved	196	.030	.010	.003	.002	.000	.000	.000	<sup>2</sup> WQC 1.0
Copper, total recoverable	113	.17	.043	.007	.003	.002	.000	.000	
Iron, dissolved	503	46	2.1	.15	.030	.010	.010	.000	
Iron, total recoverable	143	41	4.8	1.5	.44	.10	.020	.010	
Lead, dissolved	210	.12	.022	.006	.002	.000	.000	.000	MCL 0.05
Lead, total recoverable	116	.17	.036	.013	.005	.002	.000	.000	
Lithium, dissolved	29	.21	.20	.025	.010	.010	.002	.001	
Manganese, dissolved	204	5.7	.083	.017	.010	.010	.005	.000	
Manganese, total recoverable	133	.88	.063	.025	.010	.010	.010	.000	
Mercury, dissolved	145	.023	.0005	.0005	.0005	.0005	.000	.000	MCL 0.002
Mercury, total recoverable	148	.014	.0006	.0005	.0005	.0002	.0001	.0001	
Molybdenum, dissolved	24	.090	.083	.007	.001	.001	.001	.001	
Molybdenum, total recoverable	6	.007	.007	.006	.002	.001	.001	.001	
Nickel, dissolved	36	.029	.023	.002	.000	.000	.000	.000	WQC 0.0134
Selenium, dissolved	114	<sup>3</sup> .013	.008	.004	.002	.001	.000	.000	MCL 0.01
Selenium, total recoverable	74	<sup>3</sup> .006	.001	.001	.001	.001	.000	.000	
Silver, dissolved	1	.020	---	---	---	---	---	---	MCL 0.05
Silver, total recoverable	22	.002	.002	.000	.000	.000	.000	.000	
Strontium, dissolved	951	67	24	5.7	.47	.090	.001	.000	
Vanadium, dissolved	24	.67	.63	.055	.003	.000	.000	.000	
Zinc, dissolved	185	1.6	.087	.020	.010	.003	.000	.000	WQC 5.0
Zinc, total recoverable	113	.30	.15	.056	.020	.020	.003	.000	

<sup>1</sup> MCL, Maximum contaminant level for community water systems (U.S. Environmental Protection Agency, 1975).

<sup>2</sup> WQC, Water quality criteria (U.S. Environmental Protection Agency, 1980, 1981).

<sup>3</sup> Historical selenium concentrations greater than 0.005 mg/L are highly suspect; see text for discussion.

source. Only when the contaminant source might contain chemicals that form soluble complexes with the dissolved metals, or might contain chemicals that kill the naturally occurring sulfate-reducing bacteria in the system, should high concentrations of dissolved trace metals be present more than a few hundreds or thousands of feet from the source. Measurable concentrations of many trace metals can be expected to be present throughout the aquifer system, owing to the low (but nonzero) solubility of cation-hydroxide complexes (Baes and Mesmer, 1976; Stumm and Morgan, 1981, ch. 6). Fortunately, however, chemical conditions in the Floridan aquifer system are

such that high concentrations of trace metals will not normally be present.

The occurrence of stable isotopes and radioactive elements in ground water in the Upper Floridan aquifer has not been regionally investigated. Stable carbon (<sup>13</sup>C), sulfur (<sup>34</sup>S), and radiocarbon (<sup>14</sup>C) data from the Upper Floridan in peninsular Florida and coastal Georgia and South Carolina are available in published reports (Hanshaw, Back, and Rubin, 1965; Hanshaw, Back, Rubin, and Wait, 1965; Back and others, 1970; Pearson and Hanshaw, 1970; Plummer, 1977). Selected published data and new isotopic data collected during this study are

compiled in table 17; well locations for the data in table 17 are shown in figure 36. Methods for interpretation of  $^{14}\text{C}$  data have undergone considerable revision since the mid-1960's; techniques for interpreting  $^{14}\text{C}$  in hydrologic systems were recently reviewed by Mook (1980). Current methods for interpreting  $^{14}\text{C}$  require analyses of stable isotopes, especially of  $^{13}\text{C}$  and  $^{34}\text{S}$ , in the dissolved, solid, and gas phases of the system. Recent papers (Back and others, 1983; Plummer and others, 1983) discuss some of the complexities and unresolved problems of interpreting  $^{14}\text{C}$  data from carbonate aquifer systems. The techniques of the workers cited above were of limited applicability in this regional study because of the lack of data on stable isotopes in the important reacting phases. As more of the required data are collected, a better understanding of ground-water flow velocities and reaction rates in different parts of the Upper Floridan aquifer will be obtained.

Limited data on other radionuclide concentrations in the Floridan aquifer system are also available; for example, both tritium (Stringfield, 1966, p. 149–151; Pearson and Hanshaw, 1970, p. 282; Osmond and others, 1971, p. 45–54; Faulkner, 1973, p. 68–69) and uranium (U) concentrations (Osmond and others, 1968; Kaufman and others, 1969; Osmond and others, 1971, 1974; Briel, 1976; Cowart and others, 1978; Osmond, 1980) have been measured. The data reported indicate that very low or zero concentrations of tritium occur in the Floridan aquifer system, except where the system is unconfined or where sinkholes have breached thin confining units. The tritium concentrations listed below were selected from data reported by Osmond and others (1971, table 8) from wells and springs in Leon, Gadsden, and Wakulla Counties of northwestern Florida.

Sample number	Sample location	Aquifer	Casing/well depth, in feet	Tritium concentration, in tritium units
LG-01	Well #6, Tallahassee well field	Upper Floridan aquifer, semi-confined	170/413	6.1±0.5
LG-018	Well near Bradford Brook on Route 61S	Upper Floridan aquifer, semi-confined	140/220	73.8±10.8
WS-04	Wakulla Springs, sampled at 85-foot depth	Upper Floridan aquifer, unconfined	—	33.7±2.3
GG-01	Havana municipal well	Upper Floridan aquifer, confined	418/692	0±0.18

These data show typical effects of confinement on the tritium content in water samples taken from the Upper Floridan aquifer. Comparison of the tritium concentrations measured in wells LG-01 and LG-018 further illustrate the vertical stratification of water chemistry in the aquifer system. The papers cited report that dis-

solved U concentrations in the Upper Floridan aquifer are generally less than 10 parts per billion (ppb). The principal source of dissolved U in the Floridan aquifer system is phosphatic minerals (primarily apatites) that are present in the aquifer and overlying sediments. These minerals may contain as much as 75,000 ppb of U, which has been measured in apatite pellets in the Hawthorn Formation (Altschuler and others, 1958, table 19). Because the apatite content of rocks making up the Floridan aquifer system is very low, the principal source of dissolved U may be recharge through the upper confining unit, composed mostly of the Hawthorn Formation. In his summary paper, Osmond (1980) presents an overview of the principles and several examples of application of U isotopes to hydrologic studies, but he concludes (p. 261) that "confusion regarding the mechanism of fractionation, and uncertainty regarding the significance of regional variations, [have] tended to hold back progress in application [of uranium isotopes] to hydrologic problems."

A radioactive isotope of uranium, radium-226 (Ra-226), has been reported to be present in concentrations exceeding drinking water standards in a few wells and streams in southwestern Florida (U.S. Environmental Protection Agency, 1974; Irwin and Hutchinson, 1976; Kaufmann and Bliss, 1977; Sutcliffe and Miller, 1981). Irwin and Hutchinson (1976, table 1) reported results of sampling for Ra-226 in wells and streams in areas of both active phosphate mining and undisturbed phosphate deposits in central and northern Florida. They found that 5 of 30 samples from the Floridan aquifer system exceeded the recommended drinking water standard of 5 picocuries per liter (pCi/L) (U.S. Environmental Protection Agency, 1975). Sutcliffe and Miller (1981, table 1) presented data indicating that the highest Ra-226 concentrations were present in water from phosphate-rich sediments (primarily the Hawthorn and Tamiami Formations), but that deeper wells in the Upper Floridan aquifer (Ocala Limestone) contained as much as 6.3 pCi/L of Ra-226. These few results illustrate the potential mobility of U-236 and Ra-226 in ground water, and they further suggest that more analyses should be made of Ra-226 in water from the Upper Floridan aquifer in areas of known phosphate deposits.

#### TRACE ORGANIC CONTAMINANTS

Measurements by the Geological Survey of organic chemicals in the Floridan aquifer system date back to 1960, when total organic carbon was first analyzed. Early analytical techniques measured only gross quantities of organics such as oils and waxes (grease), phenols, and organic carbon in ground water (Rainwater and Thatcher, 1960; Goerlitz and Brown, 1972). As more powerful analytical tools developed, specific compounds

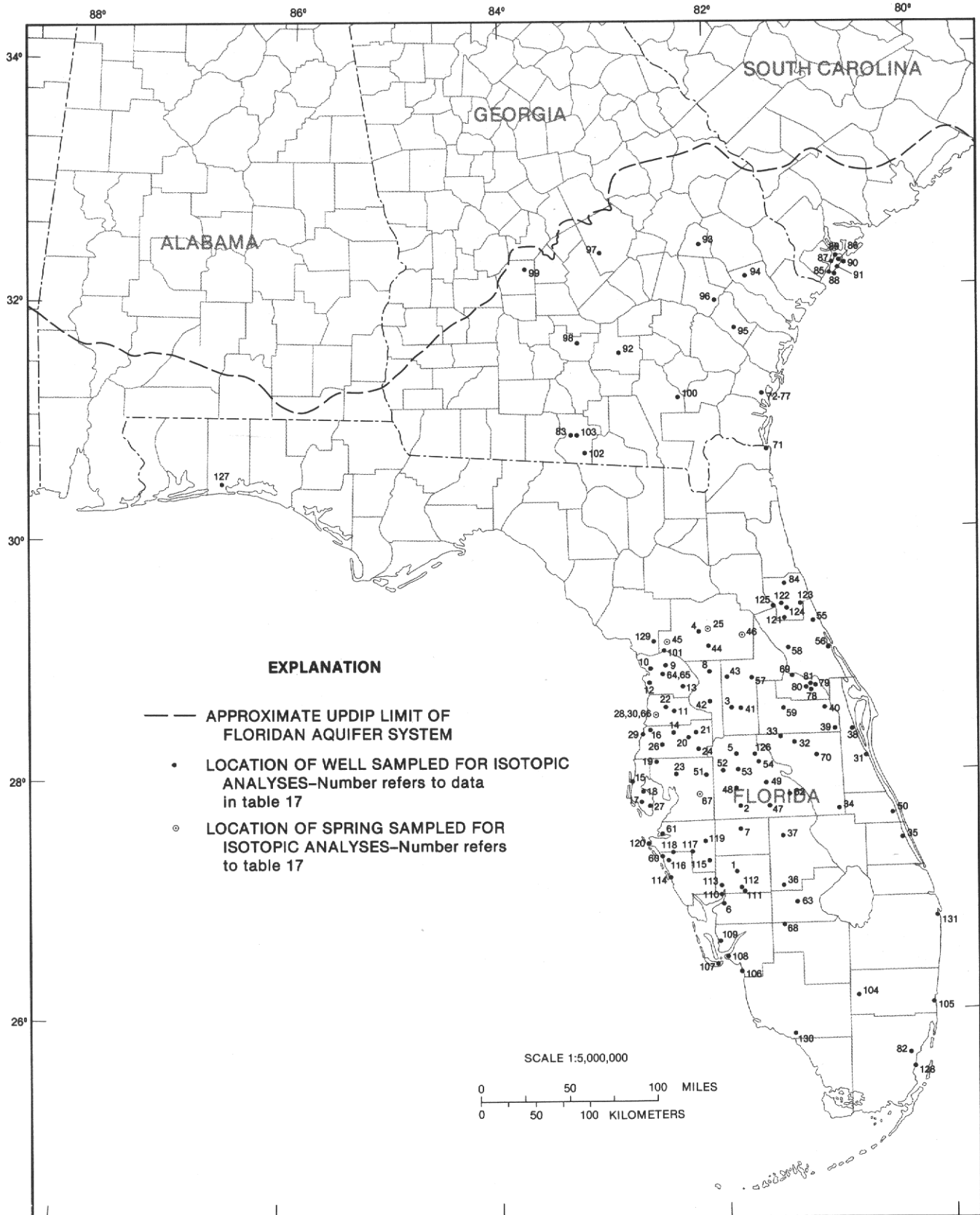


FIGURE 36.—Wells and springs in the Floridan aquifer system sampled for stable and radioactive isotopes.

TABLE 17.—Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer

[Dashes indicate no measurement]

Map number <sup>1</sup>	Well or spring name	Sample date	Stable isotope content, per thousand <sup>2</sup>				Radioactive isotope content <sup>3</sup>		Source <sup>4</sup>
			$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{34}\text{S}_{\text{SO}_4}$	$^{14}\text{C}$ , in percent modern	$^3\text{H}$ , in tritium units	
1	Arcadia	1/64	-8.3	-1.62	0.0	24.5	3.0	$0.1 \pm 1$	A, D, N
2	Fort Meade	1/64	-10.8	---	---	---	17.3	$0.2 \pm 1$	D
3	Groveland	1/64	-10.0	---	---	---	34.0	---	D
4	Ocala	1/64	-10.4	---	---	---	33.5	---	D
5	Polk City	1/64	-11.4	---	---	---	34.3	---	D
6	Cleveland	1/64	-6.0	-1.55	---	---	3.3	---	A, D
7	Wauchula	1/64	-8.5	-2.25	---	24.9	4.4	---	A, D, N
8	Wildwood	1/64	-11.3	---	---	10.5	43.6	---	D, N
9	Beverly Hills	2/65	-10.5	---	---	---	63.0	---	A
10	Crystal River	2/65	-10.5	---	---	---	44.4	---	A
11	Brooksville	2/65	-12.2	---	---	23.1	43.8	---	C, N
12	Homosassa	2/65	-10.9	---	---	---	42.4	---	A
13	Floral City	2/65	-14.9	---	---	12.5	68.3	---	A, N
14	Private well near Darby	2/65	-11.2	---	---	---	56.1	---	A
15	Clearwater	2/65	-13.6	---	---	---	40.0	---	B
16	Swartzell	2/65	-11.0	---	---	---	26.4	---	A
17	Kenneth City	2/65	-10.8	---	---	---	7.5	---	A
18	County well near High Point	2/65	-13.0	---	---	---	29.1	---	A
19	Private well near Citrus Park	2/65	-11.1	---	---	---	53.5	---	A
20	San Antonio	2/65	-10.3	---	---	9.8	45.5	---	A, N
21	Dade City	2/65	-11.9	---	---	17.7	39.4	---	A, N
22	Private well near Tooke Lake	2/65	-12.5	---	---	---	41.1	---	A
23	Temple Terrace	2/65	-11.4	---	---	---	41.8	---	A
24	Zephyrhills	2/65	-12.7	---	---	14.3	51.0	---	A, N
25	Silver Springs	2/65	-11.2	---	---	---	45.4	---	A
26	Cleveland Dairy near Drexel	2/65	-12.2	---	---	---	1.7	---	A
27	St. Petersburg	2/65	-10.5	---	---	---	26.2	---	A
28	Weeki Wachee Springs	2/65	-12.2	---	---	---	41.0	---	A
29	Hudson	2/65	-14.7	---	---	---	62.6	---	A
30	Well at Weeki Wachee Springs	2/65	-10.8	---	---	15.5	38.3	---	A, N
31	Eau Gallie	7/65	-9.9	---	---	---	4.3	---	A
32	St. Cloud	7/65	-9.8	---	---	---	9.2	---	A
33	Kissimmee	7/65	-9.3	-1.65	-0.4	---	8.4	---	A
34	Yeehaw Junction	7/65	-5.9	---	---	---	1.8	---	A
35	Fort Pierce	7/65	-2.4	-1.29	-0.2	27.4	2.1	$11 \pm 2$	A
36	Graham Dairy near Venus	7/65	-9.4	---	---	---	4.3	---	A
37	Sebring	7/65	-10.4	---	---	---	20.5	---	A
38	Cocoa	7/65	-9.3	---	---	---	7.5	---	A
39	Orange County well field	7/65	-7.3	---	---	---	1.2	---	A
40	Flowing well near Christmas	7/65	-8.9	---	---	---	5.1	---	A
41	Clermont	7/65	-10.0	---	---	---	41.6	---	A
42	Webster	7/65	-11.3	---	---	---	54.4	---	A
43	Leesburg	7/65	-10.8	---	---	8.1	33.9	---	A, N
44	Belleview	7/65	-10.0	---	---	20.4	33.4	---	A, N
45	Rainbow Springs	7/65	-9.7	---	---	---	45.1	---	A
46	Juniper Springs	7/65	-9.1	---	---	---	32.5	---	A
47	Frostproof	7/65	-9.2	-1.22	0.2	---	6.7	$0 \pm 1$	G
48	Bartow	7/65	-11.7	-2.80	---	---	43.5	---	A
49	Lake Wales	7/65	-9.4	---	---	---	20.8	---	A
50	Vero Beach	7/65	-3.6	2.12	-0.1	29.6	1.8	---	A, N
51	Plant City	7/65	-11.8	---	---	---	10.5	---	A
52	Lakeland City	7/65	-10.7	-0.50	---	---	24.9	---	A

Footnotes at end of table.

TABLE 17.—Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer—Continued

[Dashes indicate no measurement]

Map number <sup>1</sup>	Well or spring name	Sample date	Stable isotope content, per thousand <sup>2</sup>				Radioactive isotope content <sup>3</sup>		Source <sup>4</sup>
			$\delta^{18}\text{C}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{34}\text{S}_{\text{SO}_4}$	$^{14}\text{C}$ , in percent modern	$^3\text{H}$ , in tritium units	
53	Auburndale	7/65	-10.0	---	---	---	20.5	---	A
54	Haines City	7/65	-10.4	-1.20	---	---	31.8	---	A
55	Ormond Beach	7/65	-9.2	---	---	---	19.3	---	A
56	New Smyrna Beach	7/65	-10.3	---	---	---	24.5	---	A
57	Mount Dora	7/65	-10.5	---	---	---	44.9	---	A
58	Deland	7/65	-11.2	---	---	---	39.8	---	A
59	Orlando	7/65	-10.1	---	---	---	24.3	---	A
60	Sarasota	7/65	-9.1	---	---	22.8	1.2	---	A, N
61	Ellentown	7/65	-5.9	---	---	---	1.5	---	A
62	Indian Lake Estates	7/66	-10.4	---	---	---	5.8	---	A
63	Palmdale	7/66	-3.9	-1.60	---	---	0.6	0.6 $\pm$ 1	A
64	Lecanto #6 (city well)	7/66	-11.8	---	---	---	51.1	15 $\pm$ 2	G
65	Lecanto #5 (city well)	7/66	-11.5	---	0.0	---	50.0	36 $\pm$ 4	G
66	Weeki Wachee #11 (city well)	7/66	-13.7	---	-0.3	---	62.4	103 $\pm$ 16	G
67	Lithia Springs	7/66	-12.6	---	---	---	27.1	---	A
68	LaBelle	7/66	-9.8	---	---	---	1.6	---	A
69	Sanford	7/66	-10.5	---	---	---	23.9	---	A
70	Holopaw	7/66	-9.6	---	---	---	5.2	0.7 $\pm$ 1	G
71	Fort Clinch	3/67	-10.4	-0.05	---	---	---	---	A
72	Brunswick J35	2/63	---	---	-1.4 $\pm$ 0.1	---	3.5 $\pm$ 1.5	---	E
73	Brunswick D182	2/63	---	---	-1.5 $\pm$ 0.1	---	2.9 $\pm$ 1.5	---	E
74	Brunswick J11	2/63	---	---	-1.5 $\pm$ 0.1	---	2.0 $\pm$ 1.5	---	E
75	Jekyll Island J87	2/63	---	---	-1.1 $\pm$ 0.1	---	1.3 $\pm$ 1.5	---	E
76	Brunswick J12	2/63	---	---	-1.4 $\pm$ 0.1	---	2.0	---	E
77	Brunswick J77	2/63	---	---	-1.3 $\pm$ 0.1	---	3.0	---	E
78	Cockran Forest E. Well	3/82	-9.8	-3.7	---	---	31.2	---	H
79	Yarborough E. Well	3/82	-9.3	-3.8	-21.5	---	41.4	---	H
80	Cockran Forest W. Well	3/82	-10.0	-1.2	-9.0	---	4.2	---	H
81	Geneva test well	6/81	---	-3.7	-21.0	---	---	---	H
82	Kendall Lakes at 1,290 ft.	7/71	-2.0	---	---	---	5.6 $\pm$ 0.7	---	I
83	Pine Ridge near Valdosta	11/80	-13.7	-3.7	-20.0	---	---	---	L
84	ID# 293504081183601	2/82	-7.6	-2.0	---	---	<2.2	-12.5	K
85	Hilton Head Island BFT-314	4/65	-8.96	---	---	---	2.3	---	F
86	Hilton Head Island BFT-287	4/66	-12.85	---	---	---	40.0	---	F
87	Hilton Head Island BFT-317	4/66	-8.67	---	---	---	18.7	---	F
88	Hilton Head Island BFT-343	4/66	-5.06	---	---	---	1.4	---	F
89	Hilton Head Island BFT-315-190	4/65	-14.95	---	---	---	16.9	---	F
	Hilton Head Island BFT-315-483	4/65	---	---	---	---	4.0	---	F
90	Hilton Head Island BFT-407	4/66	-13.07	---	---	---	11.3	---	F
91	Hilton Head Island BFT-101-543	4/65	-6.71	---	---	---	3.5	---	F
	Hilton Head Island BFT-101-609	4/65	+0.54	---	---	---	2.1	---	F
	Hilton Head Island BFT-101-693	4/65	---	---	---	---	1.7	---	F
92	Douglas	8/81	-11.7	-4.0	-20.0	---	---	---	M
93	Metter	9/81	-9.6	-4.3	-23.0	---	---	---	M
94	Pembroke	9/81	-6.5	-3.9	-22.0	---	---	---	M
95	Ludowici	9/81	-7.2	-4.2	-21.0	---	---	---	M
96	Glennville	9/81	-9.6	-4.5	-24.0	---	---	---	M
97	Cadwell	8/81	-14.5	-4.4	-24.5	---	---	---	M
98	Ocilla	8/81	-8.9	-4.2	-21.5	---	---	---	M
99	Domestic well near Pinehurst	8/81	-10.0	-5.1	-25.5	---	---	---	M

Footnotes at end of table.

TABLE 17.—Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer—Continued

[Dashes indicate no measurement]

Map number <sup>1</sup>	Well or spring name	Sample date	Stable isotope content, per thousand <sup>2</sup>				Radioactive isotope content <sup>3</sup>		Source <sup>4</sup>
			$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{34}\text{S}_{\text{SO}_4}$	$^{14}\text{C}$ , in percent modern	$^3\text{H}$ , in tritium units	
100	Waycross test well 650–900 ft.	6/81	–12.2	–3.3	–16.0	24.1	4.4	0.3	M
	650–1,100 ft.	6/81	–12.1	–3.2	–15.5	22.3	4.3	0.3	M
	1,100–1,900 ft.	6/81	–3.0	–3.3	–17.0	---	0.0	0.1	M
	1,902–1,970 ft.	5/81	–4.7	–2.8	–14.5	---	---	0.1	M
	650–1,900 ft.	6/81	–12.4	–3.1	–17.0	23.5	16.4	0.4	M
101	Dunnellon	9/81	–9.2	–1.6	–12.0	---	45.5	---	M
102	Travel Lodge near Lake Park	11/80	–14.4	–2.55	–15.5	---	---	---	L
103	Valdosta	11/80	–14.0	–4.25	–22.0	---	---	---	L
104	Everglades test well	10/81	–1.2	–2.5	–12.0	23.1	11.9	---	M
105	Ft. Lauderdale	10/81	–2.4	–1.7	–7.5	24.4	3.1	---	M
106	Bay Beach Golf Club	7/80	–3.7	---	---	---	---	---	J
107	Private well near Sanibel	7/80	–4.4	---	---	---	---	---	J
108	Private well near East Punta Rassa	7/80	–5.1	---	---	---	---	---	J
109	Pine Island Water Association	7/80	–4.6	---	---	21.0	---	---	J
110	ROMP well near Harbor Heights	7/80	–6.4	---	---	22.4	---	---	J
111	J.R. Aborgia	7/80	–8.6	---	---	21.7	---	---	J
112	Roper Groves	7/80	–7.1	---	---	---	---	---	J
113	Gen. Devel. Corp. near Hull	7/80	–4.9	---	---	22.2	---	---	J
114	Southbay Utilities near Laurel	7/80	–7.0	---	---	21.4	---	---	J
115	Edgeville	7/80	–8.4	---	---	---	---	---	J
116	B. Jones golf course in Sarasota	7/80	–8.4	---	---	---	---	---	J
117	Verna	7/80	–6.0	---	---	21.4	---	---	J
118	Private well near Beverly Terrace	7/80	–8.6	---	---	---	---	---	J
119	Near Myakka Head	7/80	–10.2	---	---	24.2	---	---	J
120	Manatee Fruit Co. near Cortez	7/80	–10.0	---	---	---	---	---	J
121	Firetower near Cody's Corner	2/82	–11.1	–2.1	–13.0	---	35.8	---	K
122	Harper well near St. John's Park	2/82	–10.1	–1.8	–11.0	---	<3.6	---	K
123	Karona	2/82	–7.3	–1.8	–13.0	---	19.1	---	K
124	Private well near Deanville	2/82	–8.8	–0.7	–4.5	---	3.2	---	K
125	Stock well—SE of Crescent Lakes	2/84	–9.0	–1.9	–11.5	---	<6.8	---	K
126	Polk City test well 836–856 ft.	12/79	–8.8	–2.8	–13.0	---	---	---	M
	1,815 ft.	11/80	---	–3.0	–20.0	---	---	---	M
127	Fort Walton cemetery	10/79	–4.5	–4.0	–19.5	---	1.3	---	M
128	Miami	10/81	–3.9	–2.3	–11.5	22.5	6.8	---	M
129	Private well near Lebanon	9/81	–9.2	---	---	---	45.5	---	M
130	Everglades	7/66	–7.7	---	---	21.4	1.2	---	A, N
131	Peanut Island	7/66	–6.8	---	---	25.7	0.3	25.7	A, N

<sup>1</sup> Numbers refer to well locations shown in figure 36.<sup>2</sup> The  $\delta$  values are defined by 
$$\delta = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1,000.$$
For  $\delta^{13}\text{C}$ ,  $R = ^{13}\text{C}/^{12}\text{C}$ ; for  $\delta^{18}\text{O}$ ,  $R = ^{18}\text{O}/^{16}\text{O}$ ; for  $\delta^2\text{H}$ ,  $R = ^2\text{H}/^1\text{H}$ ; and for  $\delta^{34}\text{S}$ ,  $R = ^{34}\text{S}/^{32}\text{S}$ . The standards are:  $^{13}\text{C}$  - Pee Dee belemnite;  $^{18}\text{O}$  and  $^2\text{H}$  - Vienna Standard Mean Ocean Water;  $^{34}\text{S}$  - troilite from the Canyon Diablo meteorite.<sup>3</sup> Radioactive isotope activities are measured by counting the number of disintegrations per minute.  $^{14}\text{C}$  activity is reported in percent modern, relative to the activity of oxalic acid from the National Bureau of Standards:

$$^{14}\text{C} = \frac{A_{\text{sample}}}{A_{\text{ox-NBS}}} \times 100.$$

Tritium ( $^3\text{H}$ ) activity is reported in tritium units: 1 TU = 7.1 disintegrations per minute per gram water.<sup>4</sup> Data sources:

- A - Unpublished data from B. Hanshaw and W. Back, U.S. Geological Survey.  
 B - Rightmire and Hanshaw (1973).  
 C - Back and Hanshaw (1970).  
 D - Hanshaw, Back, and Rubin (1965).  
 E - Hanshaw, Back, Rubin, and Wait (1965).  
 F - Back and others (1970).  
 G - Pearson and Hanshaw (1970).  
 H - Unpublished data from G. Phelps, U.S. Geological Survey.  
 I - Unpublished data from U.S. Geological Survey files, Florida District-WRD.  
 J - Unpublished data from W. Steinkampf, U.S. Geological Survey.  
 K - Unpublished data from A. Navoy, U.S. Geological Survey.  
 L - Unpublished data from M. Baedeker, U.S. Geological Survey.  
 M - This study.  
 N - Rightmire and others (1974).



could be quantified, and more tests for possible organic contaminants in the Upper Floridan aquifer were made. The following table shows that some potential contaminants were first measured by the Geological Survey as recently as 1982.

Organic constituent measured in water samples from the Upper Floridan aquifer	Date of earliest available analysis in WATSTORE
Total organic carbon	January 1, 1960
Dissolved organic carbon	March 7, 1972
Methylene-blue active substances	January 21, 1971
Oil and grease	April 22, 1975
Phenols	May 19, 1970
Tannins and lignins	October 17, 1979
Organochlorine compounds	March 7, 1972
Organophosphorous insecticides	March 7, 1972
Chlorophenoxy-acid herbicides	March 7, 1972
Triazine herbicides	May 18, 1982
Carbamate insecticides	May 18, 1982

Given the public's increased awareness of, and concern about, ground-water contamination, testing for potential organic contaminants will probably occur with higher frequency in the future.

A statistical summary of organic chemicals measured in water samples from the Upper Floridan aquifer is presented in table 18. These data show that the majority of organic compounds were below the threshold of detection when analyzed. The data summarized in table 18 were compiled from analyses of water from wells not specifically used for artificial drainage, sewage injection, or industrial-waste disposal, in order to measure the variability and presence of organic chemicals derived from "nonpoint" sources. After wells whose names indicated an association with "point" contaminant sources were excluded, the remaining data set contained a few analyses with measurable quantities of organochlorine compounds, organophosphorous insecticides, and herbicides (table 18). This suggests that the Upper Floridan aquifer is probably susceptible to contamination by organic compounds derived from nonpoint sources.

The Upper Floridan probably is susceptible to nonpoint source contamination only in unconfined or thinly confined areas. Recently, a study was completed of the heavily irrigated agricultural area in the Dougherty Plain of southwestern Georgia, where the Floridan aquifer system is thinly confined. Hayes and others (1983) reported measurable amounts of pesticides in four wells in the Upper Floridan aquifer, but they concluded (p. 58) that "the areal extent, severity, and the long-term effects of pesticides upon the quality of water from the [Upper Floridan] cannot be determined from the available data." Wells (or springs) containing organic contaminants also are present in other parts of the aquifer system where the overlying confining unit is thin or

absent (fig. 37). An interesting feature shown in figure 37 is that wells containing organic contaminants are present in Lowndes County, Ga., where the Upper Floridan aquifer is confined. In the Lowndes County area, the aquifer receives considerable recharge from surface streams by inflow through sinkholes (Krause, 1979, p. 11-12, 23-29). Direct recharge through sinkholes (or drainage wells) reduces the possibility of biochemical or photochemical degradation of organic compounds and reduces the amount of sorption of contaminants onto clay minerals and organic matter contained in confining units. In south Georgia, once organic contaminants enter the Upper Floridan aquifer, biochemical degradation may occur, but sorption is limited by the paucity of clay minerals and organic matter in the aquifer system. In south Florida, organic contaminants were detected in three wells (fig. 37). These wells were apparently affected by wastes from nearby sewage-injection wells, as there is no possibility that a surface, nonpoint source of contamination was responsible for the organic compounds measured in these wells. The entire southern third of Florida is an area of diffuse upward leakage from the Upper Floridan aquifer (fig. 12); therefore, there is no apparent potential for contaminants from nonpoint surface sources to enter the aquifer in this area.

Disposal of sewage and waste in wells in the Floridan aquifer system has been considered for many years (for example, McCallie, 1904). Injection of treated sewage and industrial wastes in wells completed in saline parts of the Lower Floridan aquifer has increased sharply since the 1970's. Disposal of excess storm runoff via drainage wells open to the Upper Floridan aquifer (containing freshwater) is extensive in the Orlando area. The hydrologic and geochemical effects of these practices tend to be local and depend on individual well construction, aquifer hydraulic characteristics, and ground-water flow in the immediate vicinity of the well, and on the chemistry and volume of injected waste or drainage water. Therefore, the effects of these practices are described in those chapters of this Professional Paper dealing with subregional areas rather than in this regional overview of ground-water chemistry. Chapter E discusses the effects of drainage wells in the Orlando area. Chapter G describes injection of treated sewage into wells in the Miami-Palm Beach coastal area. Other papers dealing with this topic are as follows:

- Drainage wells—Kimrey (1978), Kimrey and Fayard (1982), Schiner and German (1983);
- Deep-well injection of wastes—Goolsby (1972), Kaufman and others (1973), Wilson and others (1973), Kaufman and McKenzie (1975), Ehrlich and others (1979), Meyer (1980), Vecchioli (1981), Hickey (1982), and Merritt (1983).

TABLE 18.—*Summary of organic chemicals analyzed in selected water samples from the Upper Floridan aquifer*

[Units are micrograms per liter, unless otherwise indicated. mg/L, milligrams per liter. Dashes used when compound or measure was not detected at higher percentile]

Category/Constituent	Number of samples	Maximum	95 per- centile	75 per- centile	Median	25 per- centile	5 per- centile	Minimum	Detection level	Remarks
<b>Cross measures</b>										
Carbon, organic dissolved (mg/L)	48	40	17	8.8	4.0	1.0	ND <sup>1</sup>	ND	0.1	
Carbon, organic total (mg/L)	171	35	11	6.0	1.0	ND	---	ND	0.1	
Methylene blue active substance (mg/L)	20	0.10	0.10	0.10	ND	---	---	ND	0.01	
Oil and grease, total recoverable (mg/L)	12	7	5	1	ND	---	---	ND	1	
Phenols	23	19	19	6	1	ND	ND	ND	1	
Tannins and lignins (mg/L)	8	2.0	2	2.0	1.5	0.8	0.4	0.4	0.1	
<b>Organochlorine compounds</b>										
Aldrin, total	47	ND	---	---	ND	---	---	ND	0.01	<sup>2</sup> WQC .00074
Chlordane, total	47	ND	---	---	ND	---	---	ND	0.1	WQC .0046
DDD, total	47	ND	---	---	ND	---	---	ND	0.01	
DDE, total	47	ND	---	---	ND	---	---	ND	0.01	
DDT, total	47	ND	---	---	ND	---	---	ND	0.01	WQC .00024
Dieldrin, total	47	0.02	ND	---	ND	---	---	ND	0.01	
Endosulfan, total	24	ND	---	---	ND	---	---	ND	0.01	WQC .00071
Endrin, total	47	ND	---	---	ND	---	---	ND	0.01	<sup>3</sup> MCL 0.2; WQC 1
Heptachlor, total	47	ND	---	---	ND	---	---	ND	0.01	WQC .00278
Heptachlor epoxide, total	47	ND	---	---	ND	---	---	ND	0.01	
Lindane, total	47	ND	---	---	ND	---	---	ND	0.01	MCL 4.0
Methoxychlor, total	28	ND	---	---	ND	---	---	ND	0.01	MCL 100
Mirex, total	15	ND	---	---	ND	---	---	ND	0.01	
Perthane, total	23	0.1	0.1	0.1	ND	---	---	ND	0.1	
Polychlorinated biphenyls, total	47	ND	---	---	ND	---	---	ND	0.1	WQC .00079
Polychlorinated naphthalenes, total	36	ND	---	---	ND	---	---	ND	0.1	
Toxaphene, total	47	1.0	1.0	ND	ND	---	---	ND	0.01	
<b>Organophosphorous insecticides</b>										
Diazinon, total	9	0.02	0.02	ND	ND	---	---	ND	0.01	
Ethion, total	9	ND	---	---	ND	---	---	ND	0.01	
Malathion, total	9	ND	---	---	ND	---	---	ND	0.01	
Methyl parathion, total	9	ND	---	---	ND	---	---	ND	0.01	
Methyl trithion, total	9	ND	---	---	ND	---	---	ND	0.01	
Parathion, total	9	ND	---	---	ND	---	---	ND	0.01	
Trithion, total	9	ND	---	---	ND	---	---	ND	0.01	
<b>Chlorophenoxy acid herbicides</b>										
Silvex, total	38	0.36	0.02	ND	ND	---	---	ND	0.01	
2, 4-D, total	38	0.02	.01	ND	ND	---	---	ND	0.01	MCL 100
2, 4, 5-T, total	38	ND	---	---	ND	---	---	ND	0.01	MCL 10
<b>Triazine herbicides</b>										
Atrazine, total	10	ND	---	---	ND	---	---	ND	0.1	
Prometone, total	10	ND	---	---	ND	---	---	ND	0.1	
Prometryne, total	10	ND	---	---	ND	---	---	ND	0.1	
Propazine, total	10	ND	---	---	ND	---	---	ND	0.1	
Simazine, total	10	ND	---	---	ND	---	---	ND	0.1	
Simetryne, total	10	ND	---	---	ND	---	---	ND	0.1	
<b>Carbamate insecticides</b>										
Methomyl, total	10	ND	---	---	ND	---	---	ND	0.5	
Propham, total	10	ND	---	---	ND	---	---	ND	0.5	

<sup>1</sup> ND, Constituent below the threshold of detection.<sup>2</sup> WQC, Water-quality criteria (U.S. Environmental Protection Agency, 1980, 1981).<sup>3</sup> MCL, Maximum contaminant level for community water systems (U.S. Environmental Protection Agency, 1975).

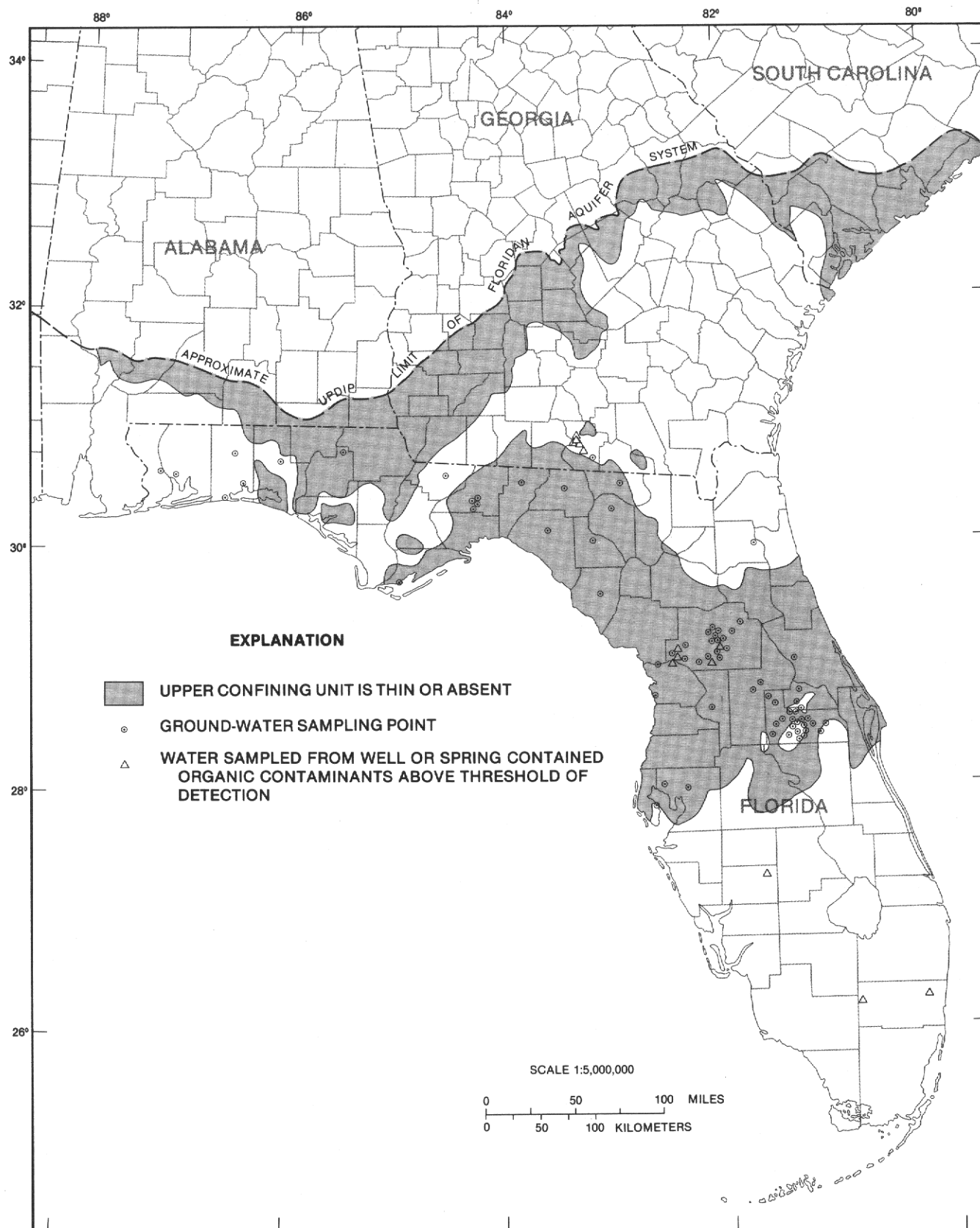


FIGURE 37.—Wells and springs in the Upper Floridan aquifer sampled for organic contaminants.